Publication No. 41

The British Research Association
for the
Woollen and Worsted Industries

The Changes of Weight and Moisture Absorbing Power Produced by Dyeing and Allied Processes

By
S. A. SHORTER, H. R. HIRST and W. J. HALL.

It is requested that publications be kept in the personal control of a Director or head of the firm, and not lent to or discussed with other than those responsible managers, etc., necessarily informed for the conduct of the business.

December, 1924

BRITISH RESEARCH ASSOCIATION
for the
WOOLLEN AND WORSTED INDUSTRIES,
Torridon, Headingley, LEEDS.

SENIOR STAFF.

DIRECTOR OF RESEARCH : H. J. W. Bliss, M.A., F.I.C.

SECRETARY : Arnold Frobisher, B.Sc., F.S.S.

Departments :

PHYSICS : S. A. Shorter, D.Sc.
(Assist.) W. J. Hall, B.Sc., A.R.C.S.

COLLOIDS : S. A. Shorter, D.Sc.

CHEMISTRY : H. R. Hirst, B.Sc., F.I.C.
A. T. King, B.Sc., F.I.C.
(Assist.) J. Barritt, B.Sc., A.R.C.S.

BIOLOGY : *

ENGINEERING : A. W. Stevenson, B.Sc., Wh.Ex.

WOOLLEN CARDING & SPINNING : Percy Jowett.

WORSTED SPINNING : Howard Priestman.

CONSULTING : Howard Priestman.

*Dr. F. A. E. Crew, Director of the Animal Breeding Research Department, The University, Edinburgh, has kindly offered to co-operate with the Association.

The British Research Association
for the
Woollen and Worsted Industries

The Changes of Weight and Moisture Absorbing Power Produced by Dyeing and Allied Processes

By
S. A. SHORTER, H. R. HIRST and W. J. HALL.

December, 1924

BRITISH RESEARCH ASSOCIATION
for the
WOOLLEN AND WORSTED INDUSTRIES,
Torridon, Headingley, LEEDS.

Terms Used in this Publication.

A brief explanation is given herewith. For a fuller description of those concerning regain, see Publication No. 38, p. 22.

Regain.

The amount of moisture contained in cloth, etc., calculated as a percentage of the dry weight.

Equilibrium Regain.

The amount of moisture absorbed in a given atmosphere. In this paper the atmosphere of the humidity room (which is fixed and controlled), is generally referred to.

Hygroscopic Capacity.

Power of absorbing moisture. Some samples have a greater power and some less, according to treatment. They therefore take up a bigger or a less equilibrium regain.

Condition. Conditioned.

Wool is said to be conditioned when it is moistened or allowed to absorb moisture, usually to the amount of the recognised standard, or to a state of equilibrium with a standard atmosphere.

The Changes of Weight and Moisture Absorbing Power

Produced in Dyeing and Allied Processes

1. INTRODUCTION.

A study of this Publication and No. 32 together will help the dyer and manufacturer (a) to select the methods of dyeing most likely to give a full finished weight, (b) to calculate from the loom weights so as to give instructions for finishing to correct regain and weight.

The present work arose out of the problem discussed in Publication No. 32, which deals with the question of the finishing of pieces to correct weight according to the Conditioning House standard of 16% regain.

The object of the work is to investigate the losses or gains of weight resulting from dyeing, so that manufacturers will be in a better position to calculate more accurately the finished weights of their pieces. The results of the work also indicate which classes of dyestuffs give the best yield of finished cloth.

The changes of weight have been determined in two different ways. We have determined, first, the change of absolute dry weight, and secondly, the change of weight in an atmosphere of definite humidity. The second method corresponds to what would be obtained by weighing in the mill if one could be certain of steady atmospheric conditions.

These two methods of calculation do not necessarily yield the same result in any particular instance. Only in the exceptional case where the dyeing process does not affect the hygroscopic capacity (power of absorbing moisture) do both methods give the same result. In general the dyeing alters the power of absorbing moisture so that two samples (one undyed and the other dyed) placed side by side in the same atmosphere would naturally absorb different percentages of moisture.

The most striking examples of such a change of hygroscopic capacity (power of absorbing moisture) are afforded by pieces dyed with acid dyes. Such pieces gain considerably in dry weight but at the same time suffer a loss of hygroscopic capacity so marked that the weight in an ordinary atmosphere shows very little increase and may even show a loss.

The power of absorbing moisture is also reduced by drying at a high temperature (as in tentering), and by hot pressing (see Publication No. 33). This effect will be additional to that due to dyeing so that it is possible to get an actual reduction of ordinary weight by an acid dyeing in spite of the increase of dry weight.

For a summary of the results see p. 9.

The Practical Application of the Results.

We have three weights to deal with :—

(a) The dry weight including the loss or gain in dyeing.

(b) The weight at standard regain, that is the dry weight plus 16% (for wool fabrics, other than hosiery).

(c) The weight at what may be termed the natural regain in an ordinary atmosphere. This may be either more or less than (b).

Now Publication No. 32 and this Publication together show how to finish to correct weight (b). This can nearly always be done without difficulty.

But if weight (c), the natural weight, is much less than (b), then the cloth *may* feel too damp if brought up to the 16% and may be too liable to lose weight in the warehouse, etc. Table V., Sample No. 29 might be such a case, and cloth containing much cotton will also be troublesome, as cotton has a much less natural regain than wool.

The thanks of the Association are due to Messrs. Hawley & Johnson Ltd., Messrs. Wm. Kitchen & Co., Messrs. G. H. Hirst & Co. Ltd., and Messrs. J. C. Waddington & Sons, for their work in carrying out dyeings, etc.

2. LABORATORY EXPERIMENTS.

The laboratory experiments were all conducted with hosiery web knitted on a stocking frame from 1/24's botany yarn, of about 60's quality. In this form the yarn is easily manipulated without risk of losing material. Long lengths of web were knitted and scoured carefully by hand, the washing off being very thorough. The percentage of total alkali left in the material was found by titration to be equivalent to 1.52% of soap.* The web was then cut into pieces of suitable size and these were hung in the humidity room to attain a steady state (as shown by weighing on consecutive days). The dry weight of one of the samples was then determined, and from this the dry weights of the other samples before dyeing or similar treatment were calculated (by simple proportion).

After the treatment the samples were returned to the humidity room, and when in a steady state, each sample was divided into two roughly equal parts (both accurately weighed), of which one was dried out and the other (whose dry weight could be calculated) used for determination of the equilibrium regain in atmospheres of different humidity.

The samples weighed about 25 grm. each and they were treated in about 1500 c.c. of liquor. These proportions are about the same as in large scale dyeings.

* All the material was scoured so as to give a cloth closely equivalent to an average commercial scour as proved by the analysis.

Boiling Water.

In Table I. are given data relative to the effect of boiling in water.

It will be seen that the process of boiling in water causes a loss of dry material, as is to be expected. The greater effect of distilled water as compared with Leeds Town water may be noted.

The effect on the hygroscopic capacity will depend very much on the previous treatment of the material. Thus a hot-pressed sample of hosiery web might have its equilibrium regain increased as much as 3% by boiling in water (see Publication 33). In the case of a sample which had not received any extreme treatment (tentering, hot-pressing, etc.), we should expect very little effect. Actually the results given by Samples 2 and 3 show differences which are within the limits of experimental error.

Sulphuric Acid, and Bleaching Agents.

Table II. contains the results of a series of measurements on samples treated with sulphuric acid, and also on samples bleached in different ways. It will be seen that the samples treated with acid have shown a gain of dry material (as is to be expected). There is, however, a marked decrease in the capacity for absorbing moisture so that this dry weight increase is nullified when the material is weighed in an ordinary atmosphere.

The gain of weight on treatment with acid is, of course, due to the well-known affinity of wool for acid. On rinsing wool which has been acidified, the acid at first is readily removed, but a stage is reached when the rate of removal is extremely slow, so that for practical purposes it may be said that the acid cannot be completely removed by rinsing.

The amount of acid left on will thus depend to some extent upon the degree of rinsing.

It is worthy of note that bleaching with hydrogen peroxide causes a gain of weight, while bleaching with sodium peroxide causes a loss.

For further results with sulphuric acid see Table VI. and pp. 25 to 27.

It will be noted that formic and acetic acids do not reduce the hygroscopic capacity to the same extent as sulphuric acid.

Chrome.

Table III. relates to treatment with potassium bichromate. Samples 15 and 16 correspond to ordinary chroming while 17 has had a severer treatment with acid such as would be used for stripping. Samples 15 and 16 have lost in dry weight. Their hygroscopic capacity has not been much affected, so that the losses of conditioned weight do not differ much from the losses of dry weight. Sample 17 has gained appreciably in dry weight, but owing to the loss of hygroscopic capacity the gain of conditioned weight is much less.

It will be seen that the loss due to the bichromate (15) is diminished by the addition of bitartrate.

The gain when sulphuric acid is used in addition to the bichromate is evidently the resultant of a loss due to the latter, and a gain due to the former. As in the case of the simple absorption of acid, the gain is accompanied by a marked loss of hygroscopic capacity (moisture absorbing power) so that the gain in weight in an ordinary atmosphere is small.

No. 17 cannot, of course, be compared with No. 15 as the time of boiling is less, and there would be practically no reduction of the chromic acid with consequent loss of wool substance.

Stripping.

The effect of various stripping agents is shown in Table IV. The samples treated with formosol have suffered a loss of dry weight. In addition there has been a loss of moisture absorbing power, so that when weighed in an ordinary atmosphere the samples have shown a % loss of weight greater than the loss of dry weight.

The treatment with permanganate, etc., has given no change of dry weight. This is evidently a balance of losses and gains.

Boiling with ammonia has caused a considerable loss of dry weight. There has also been a slight increase of moisture absorbing power possibly owing to the removal of relatively non-hygroscopic matter (dirt, grease). In other words the ammonia has effected a scour. (See Publication No. 38, p. 14).

Acid Dyes.

Table V. contains results relating to samples dyed with acid dyes.

It will be seen that in all cases there is a gain of dry weight. On the other hand there is always a considerable diminution in the moisture absorbing power, so that the weights in an ordinary atmosphere show a diminished gain or even a loss.

Some of the experiments have been performed in duplicate for the purpose of testing the accuracy of the method adopted, e.g., 29 and 30 ; 31 and 32. The agreement in the case of these two pairs of duplicates is as close as can reasonably be expected in view of the nature of the treatment, chemical and mechanical, which the material undergoes.

In order to investigate the question of sulphuric acid and Glauber salts a series of experiments were carried out. The results of these are shown in Table VI.

Sulphuric Acid and Glauber's Salts, and Effect of Washing Off.

Table VI.* contains the results of two series of experiments on the effect of boiling (a) with sulphuric acid alone, (b) with sulphuric acid and Glauber's salts, (c) with sulphuric acid, Glauber salts and

* Printed in the Appendix.

Crystal Scarlet. The experiments constitute a more detailed investigation of some of the cases dealt with in Tables II. and V.

In these experiments measurements were made of (1) the amount of acid remaining in the bath after dyeing, (2) the amount in the fabric after washing and dyeing. From these figures can be calculated the amount taken up by the fabric at the boil and the amount washed off. In order to remove the acid liquor merely entangled with the fabric, we squeezed and rinsed the fabric twice in distilled water, the liquor squeezed out being returned to the bath. The subsequent washing off was conducted in a large volume of running tap water for half an hour.

The results are in fair agreement with the previous results, so far as they are comparable with them. There are many other interesting features which will be dealt with in the appendix.

It will be seen that Glauber's salts have little or no effect on the amount of acid absorbed, nor on the dry weight. The solutions are, of course, very dilute.

Various Dyes.

Table VII. contains the results of experiments with a number of different kinds of dye. It will be seen that in nearly all cases the treatment has caused very little change of hygroscopic capacity so that the changes of conditioned weight do not differ much from the changes of dry weight. These samples show in this respect a marked difference from those dyed with acid colours.

In connection with this loss of hygroscopic capacity in dyeing with acid colours, it may be pointed out this effect only applies to piece dyeing. The effect of subsequent scouring (such as would occur after loose wool, slubbing or yarn dyeing) may probably be to restore the hygroscopic capacity, though at the same time to cause a net loss of weight owing to the neutralisation or removal of the excess of acid. This will be investigated later.

3. LARGE SCALE EXPERIMENTS.

Samples were prepared in a manner similar to that adopted in the laboratory experiments, so that the dry weights previous to dyeing were known. The samples were then sent to the works where they were attached to pieces and dyed in the ordinary way with precautions to prevent gross losses of material.

The following series of experiments were carried out with :—

(1) Twelve 2 yd. lengths of 9 oz. worsted cloth. See Table VIII. (2/60's warp of 64/70's quality : single weft of 56's quality).

(2) Twelve 2 yd. lengths of medium woollen cloth. See Table IX.

(3) Twelve 2 yd. lengths of medium woollen cloth. See Table X.

(4) Five tests of 2 yd. lengths of cotton warp shoddy. See Table XI.

Some lengths of hosiery fabric were also sent to a hosiery dyer, thus forming a fifth series.

(5) Twelve tests on 2 yd. lengths of tubular botany web of about 64's quality. See Table XII.

The changes in dry weight are in agreement with the results of the small scale experiments, so that in the latter the conditions prevailing in large scale dyeing have been fairly accurately reproduced.

Effect of Finishing, etc.

The changes of conditioned weight are subject to greater uncertainty owing to our lack of knowledge of the precise treatment of the material. Thus the samples dealt with in Table IX. show a very low regain after dyeing. This is almost certainly due to their having been dried at a high temperature before their return to us.* On the other hand the samples dealt with in Table X. were returned to us wet, and were dried by us without heat. It will be seen that the equilibrium regains are much larger.

The low regains after complete finishing shown in Table XII. are evidently due to the hot-pressing (see Publication No. 33). On wetting out, the samples show a marked increase of hygroscopic capacity, some of them becoming more hygroscopic than before dyeing. The explanation of this is that the original web had received a mild pressing and had its hygroscopic capacity lowered. The samples of worsted cloth (Table VIII.) show a low initial hygroscopic capacity, but a certain amount of recovery takes place during finishing.

Comparative Effect of Sulphuric and Other Acids.

In spite of these complications, the results again show that material dyed in the presence of sulphuric acid has a diminished hygroscopic capacity. Thus the regains of the hosiery samples (Table XII.) after wetting out, classified according to the nature of the addition to the bath are† :—

Sulphuric Acid.	Formic Acid.	No addition.
13.52	13.74	14.30
13.06	14.50	
13.15		
13.24		
13.20		
12.83		
13.50		
14.07		
12.71		
Mean 13.25	14.12	

* The effect of cloth finishing processes on the hygroscopic capacity is at present under investigation. See also Publication 33.

† The values of the regain are those obtained after wetting out the samples (thus eliminating largely the effect of hot-pressing). The lower values obtained with the samples just as they came from the dyers gave the following results :—

Mean value of regain of samples dyed with addition of sulphuric acid=12.62
do. formic acid =13.37
do. without addition of acid =13.80

The same differences are shown in Table VIII. Classifying in a similar way we have :—

	Sulphuric Acid.	Acetic Acid.	No acid—indigo.
	13.72	14.54	14.96
	13.13	14.60	14.76
	13.28	14.84	14.42 (bottomed)
Mean	13.38	14.66	14.86 (mean of first two)

Sulphuric acid, of course, though it produces a diminution of hygroscopic capacity, which adversely affects the weight in an ordinary atmosphere, gives a greater dry weight than formic or acetic acids.

In Tables IX. and X. the results for each dye are given twice. In each table the first six results relate to a portion of the cloth which was milled with potash olive-oil soap and the second six to a portion which was milled with hard soda soap.

SUMMARY.

Sulphuric acid gives an increase in bone dry weight. There is, however, a diminution of hygroscopic capacity, so that when weighed in an ordinary atmosphere, the sample shows a much diminished gain in weight, and may even show (especially if the sample be hot pressed) an actual loss of weight.

Acetic and formic acids do not produce this large diminution of hygroscopic capacity, though, of course, they give a less gain of dry weight.

Also, as is well known in the trade, indigo gives an excellent increase in dry weight of the cloth, and, moreover, this increase is fully maintained in an ordinary atmosphere.

Diamond black gives less weight than Logwood black.

Logwood appears to maintain any increase in weight when it has assumed its natural moisture.

Acid blacks on the other hand give a large increase in dry weight, but when exposed to ordinary atmosphere this proves to be largely fictitious. The dye produces an increase in weight in addition to that due to absorption of acid.

It is, however, difficult to dye shades with different classes of dyes which will be strictly comparable in depth of shade, so that with these blacks we have laid more stress on the ability to retain moisture than on the actual increases in weight from the undyed state.

Excessive washing off with acid dyes will cause a reduction in the gain of dry weight.

TABLE I.—(Effect of Boiling Water).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of		Change of conditioned weight as measured in atmosphere of	
			59% Hm. (72°F.)	84.5% Hm.	59% Hm. (72°F.)	84.5 %Hm.
1	None	—	(15.47%)	(21.12%)	—	—
2	Boiled in water* for 1 hr.	0.37% loss	15.63%	21.00%	0.23% loss	0.47% loss
3	Boiled in water for 2 hrs.	0.48% loss	15.85%	20.95%	0.16% loss	0.62% loss
4	Distilled water, ½ hr. to boil, 1 hr. boiling, ½ hr. wash off	1.43% loss	—	—	—	—
5	Boiled in four separate lots of distilled water (1 hr. total boil)	1.50% loss	—	—	—	—
6	Dried in conditioning oven at 230°F., then boiled 1 hr. in dist. water	1.23% loss	—	—	—	—

*Leeds Town

TABLE II.—(Effect of H_2SO_4 and Bleaching Agents).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of		Change of conditioned weight as measured in atmosphere of	
			59% Hm. (72°F.)	84.5% Hm.	59% Hm. (72°F.)	84.5% Hm.
1	None	—	(15.47%)	(21.12%)	—	—
7	Boiled 1 hr. in 4% Sulphuric Acid, ½ hr. wash off	0.72% gain	13.40%	19.42%	1.08% loss	0.69% loss
8	Boiled 1 hr. in 4% Sulphuric Acid + 10% Glauber's Salts, ½ hr. wash off	0.50% gain	14.52%	19.72%	0.33% loss	0.66% loss
9	Bleached by exposure to fumes from burning sulphur, ½ hr. wash off	1.01% gain	14.22%	18.43%	0.09% loss	1.23% loss
10	Bleached over Sulphurous Acid soln., ½ hr. wash off	1.01% gain	14.20%	18.61%	0.10% loss	1.08% loss
11	Bleached in Sulphurous Acid soln., ½ hr. wash off	0.92% gain	14.00%	18.48%	0.36% loss	1.28% loss
12	Excessive treatment as 9, no wash off	2.23% gain	—	—	—	—
13	Bleached with Hydrogen Peroxide soln. (5% soln. of 20 vol. hyd. perox. made slightly alkaline with ammonia)	0.61% gain	—	—	—	—
14	Bleached with Sodium Peroxide and Sulphuric Acid (0.41% sod. perox.) (0.56% H_2SO_4)	2.19% loss	—	—	—	—

TABLE III.—(Effect of Potassium Bichromate).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of		Change of conditioned weight as measured in atmosphere of	
			59% Hm. (72 °F.)	84.5% Hm.	59% Hm. (72 °F.)	84.5% Hm.
1	None	—	(15.47%)	(21.12%)	—	—
15	3% Pot. Bichromate, ½ hr. to boil, 1½ hrs. boiling, ½ hr. wash off	0.42% loss	15.28%	21.10%	0.58% loss	0.44% loss
16	3% Pot. Bichromate, 2½% Pot. Bitartrate; ½ hr. to boil, 1½ hrs. boiling, ½ hr. wash off	0.10% loss	15.23%	20.81%	0.31% loss	0.36% loss
17	5% Pot. Bichromate, 10% Sulphuric Acid; ¾ hr. to boil, 5 mins. boiling, ½ hr. wash off	2.24% gain	14.38%	19.60%	1.27% gain	0.96% gain

TABLE IV.—(Effect of Stripping Agents).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of		Change of conditioned weight as measured in atmosphere of	
			59% Hm. (72°F.)	84.5% Hm.	59% Hm. (72°F.)	84.5% Hm.
1	None	—	(15.47%)	(21.12%)	—	—
18	4% Formosol (Brotherton) ½ hr. to boil, 2% Formic Acid (75%) ½ hr. boiling, ½ hr. wash off	1.14% loss	14.53%	19.23%	1.95% loss	2.68% loss
19	4% Formosol ½ hr. to boil, 2½% Acetic Acid (50%) ½ hr. boiling, ½ hr. wash off	0.44% loss	14.20%	19.48%	1.53% loss	1.79% loss
20	5% Ammonia (0.96 sp. gr.) ½ hr. to boil, 10 mins. boiling, ½ hr. wash off	2.16% loss	15.61%	21.04%	2.04% loss	2.22% loss
21	4% Pot. Permanganate followed by 10% Bisulphite 3% Sulphuric Acid } at 116°F.	no change	13.89%	19.70%	1.37% loss	1.17% loss

For bichromate see Table III.

TABLE V.—(Effects with Acid Dyes).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of 59% Hm. (72°F.)	Regain in atmosphere of 84.5% Hm.	Change of conditioned weight as measured in atmosphere of 59% Hm. (72°F.)	Change of conditioned weight as measured in atmosphere of 84.5% Hm.
1	None	—	(15.47%)	(21.12%)	—	—
22	3% Orange 2 G 4% Sulphuric Acid 10% Sod. Sulphate } ½ hr. to boil, 1 hr. boiling, ½ hr. wash off	1.45% gain	13.70%	18.37%	0.10% loss	0.85% loss
26	.05% Scarlet 6 R 4% Sulphuric Acid 20% Sodium Sulphate } usual dyeing	1.54% gain	13.70%	19.73%	Nil	0.37% gain
27	.3% Scarlet 6 R 4% Sulphuric Acid 10% Sodium Sulphate } usual dyeing The gain in this case is exceptionally low, possibly due to more complete washing off (see Appendix).	0.50% gain	13.63%	18.62%	1.10% loss	1.56% loss
28	.3% Scarlet 6 R 4% Formic Acid (75%) 10% Sod. Sulphate } usual dyeing	0.22% gain	14.54%	19.63%	0.59% loss	1.02% loss
29	5% Scarlet 6 R 4% Sulphuric Acid 20% Sod. Sulphate } usual dyeing	4.90% gain	11.88%	17.35%	1.64% gain	1.64% gain
30	Same treatment as No. 29	4.77% gain	—	—	—	—
31	10% Scarlet 6 R 4% Sulphuric Acid 20% Sod. Sulphate } usual dyeing (incomplete exhaustion) A repetition of the dyeing gave 0.25% colour remaining in the bath, i.e., 1/40th of original colour.	7.49% gain	—	18.52%	—	5.18% gain
32	Same treatment as No. 31	7.88% gain	—	—	—	—

TABLE V.—*continued.*

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of 59% Hm. (72 °F.)	Regain in atmosphere of 84.5Hm.	Change of conditioned weight as measured in atmosphere of 59% Hm. (72 °F).	Change of conditioned weight as measured in atmosphere of 84.5% Hm.
33	3% Scarlet 6 R 4% Sulphuric Aci 20% Sod. Sulphate } ½ hr. to boil, 1 hr. boiling, ½ hr. to wash off. Left wet overnight then	2.27% gain	—	—	—	—
	4% Formosol 2.5% Acetic Acid } ¾ hr. to boil, 20 mins. boiling, wash off in cold water ½ hr. Wash in warm water 10 mins.					
	put through wringer then 1% Scarlet 6 R 4% Sulphuric Acid 20% Sod. Sulphate } 35 mins. to boil, 1 hr. boiling, ½ hr. wash off					
38	10% Napthalene Black B.D. 4% Sulphuric Acid 10% Sod. Sulphate } usual dyeing	4.39% gain	—	18.76%	—	2.35% gain
39	10% Napthalene Black B.D. boiled 10 mins. cooled, added 4% Sulphuric Acid 10% Sod. Sulphate } usual dyeing	3.45% gain	—	19.26%	—	1.86% gain
43	3% Coomassie Navy Blue 2 RNX 3% Amon. Acetate 20% Sod. Sulphate } boil ¾ hr., add 1% Acetic Acid (50%), ¼ hr. boiling, wash off	0.51% gain	—	—	—	—

TABLE VII.

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of 59% Hm. (72°F.)	Regain in atmosphere of 84.5% Hm.	Change of conditioned weight as measured in atmosphere of 59% Hm. (72°F.)	Change of conditioned weight as measured in atmosphere of 84.5% Hm.
1	None	—	(15.47%)	(21.12%)	—	—
23	3% Pot. Bichromate, ½ hr. to boil, 1½ hrs. boiling, ½ hr. to wash off, then 5% Aliz. Orange HO, 25 mins. to boil, after boiling ½ hr. add 1% of 50% Acetic Acid, boil 1 hr. (total 1½ hrs.), ½ hr. wash off	0.84% gain	14.45%	19.70%	Nil	0.32% loss
24	3% Pot. Bichromate, 2½% Pot. Bitart. } boil and wash off as usual, then Aliz. Orange as No. 23	0.68% gain	14.62%	20.18%	0.06% loss	0.10% loss
25	2% Benzopurpurine, 20% Sod. Sulphate } ½ hr. to boil, 1½ hrs. boiling, ½ hr. wash off	1.56% loss	15.64%	21.12%	1.36% loss	1.56% loss
34	5% Metachrome Brown, 5% Metachrome Mordant } raise to boil 1 hr. 1½ hrs. boiling, ½ hr. wash off	0.37% gain	14.51%	21.04%	0.47% loss	0.30% gain
35	1% Metachrome Brown, 3% Metachrome Mordant } Same treatment as No. 34	0.54% loss	14.79%	21.33%	1.13% loss	0.37% loss
36	3% Bichrome, 1% Sulphuric Acid } ½ hr. to boil, 1¼ hrs. boiling, ½ hr. wash off, then 8% Hematine Xt., ½ hr. to boil, 1 hr. boiling, ½ hr. to wash off	3.12% gain	15.03%	21.80%	2.73% gain	3.70% gain

TABLE VII.—*continued.*

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of		Change of conditioned weight as measured in atmosphere of	
			59% Hm. (72 °F.)	84.5% Hm.	59% Hm. (72 °F.)	84.5% Hm.
37	3% Bichrome, ½ hr. to boil, 1¼ hrs. boiling, ½ hr. wash off, then 8% Hematine Xt., ½ hr. to boil, 1 hr. boiling, ½ hr. wash off	2.63% gain	15.80%	21.98%	2.93% gain	3.36% gain
40	8% Eriochrome Black P.B. (conc.) 3% Acetic Acid 10% Sod. Sulphate Enter at 50°C., raise to boil ¾ hr., ½ hr. boiling, add 1.5% Pot. Bichrome, ½ hr. boiling, ½ hr. wash off	3.14% gain	—	21.00%	—	2.94% gain
41	8% Eriochrome Black A. Treatment as No. 40	2.35% gain	—	21.40%	—	2.58% gain
42	7% Solochrome Black T. 2.5% Acetic Acid 10% Sod. Sulphate ¾ hr. boiling, add 2.5% chrome, ½ hr. boiling, wash off	3.39% gain	—	21.05%	—	3.33% gain

TABLE VIII.—(9 oz. Worsted Cloth).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of 59% Humidity (72°F.)			Change of conditioned weight as measured in an atmosphere of 59% H. (72°F.)	
			Before treatment	After treatment	After complete finishing	After treatment	After complete finishing
44	Logwood Black on chrome	2.24% gain	—	—	—	—	—
45	Same as 44—burl dyed tannin and iron	2.51% gain	—	—	—	—	—
46	Blue, Indigo, pure, medium shade	3.85% gain	13.84%	13.87%	14.96%	3.74% gain	4.89% gain
47	Blue, with red bottom on chrome, full shade	5.08% gain	,,	13.74%	14.76%	4.85% gain	5.82% gain
48	Blue, Indigo, topped with chrome colour, full shade	4.17% gain	,,	13.25%	14.42%	3.66% gain	4.71% gain
49	Grey, acid colour pale with Acetic Acid	0.16% loss	,,	13.16%	14.54%	0.74% loss	0.49% gain
50	Light Grey, acid colour pale with Sulphuric Acid	1.16% gain	,,	13.28%	13.72%	0.63% gain	1.07% gain
51	Light Blue, acid colour, full shade, with Acetic Acid	0.61% gain	,,	13.23%	14.60%	0.05% gain	1.29% gain
52	Brown, acid colour, full shade, with Sulphuric Acid	2.65% gain	,,	12.15%	13.13%	1.10% gain	2.02% gain
53	Acid Black (Sulphuric Acid)	4.34% gain	,,	12.44%	13.28%	3.04% gain	3.83% gain
54	Blue, after chrome blue (navy) (Acetic Acid)	1.78% gain	,,	13.72%	14.84%	1.73% gain	2.68% gain
55	Black, Diamond Black (Acetic Acid)	2.80% gain	,,	13.51%	14.60%	2.48% gain	3.49% gain

TABLE IX.—(Medium Woollen Cloth).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of 59% Humidity (72°F.)		% change of conditioned weight as measured in atmosphere of 59% H., after treatment.
			Before treatment	Sample tentered but not completely finished	
68	Acid Black	7.95% gain	14.24%	11.68%	5.53% gain
69	Logwood Black	4.58% gain	,,	12.52%	3.05% gain
70	Navy	1.63% gain	,,	11.80%	0.48% loss
71	Stripped and dyed fawn	4.82% loss	,,	12.54%	6.18% loss
72	Fawn	0.41% gain	,,	12.44%	1.05% loss
73	Indigo	1.86% gain	,,	13.19%	1.00% gain
74	Acid Black	8.25% gain	14.06%	11.34%	5.70% gain
75	Logwood Black	4.96% gain	,,	12.54%	3.61% gain
76	Navy	4.58% gain	,,	11.80%	2.50% gain
77	Stripped and dyed fawn	1.27% loss	,,	12.41%	2.62% loss
78	Fawn	0.25% gain	,,	12.56%	1.05% loss
79	Indigo	1.66% gain	,,	13.31%	1.04% gain

Milled—First six with soft soap. Second six with hard soap.

TABLE X.—(Medium Woollen Cloth).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of 59% Humidity (72°F.)		% change of conditioned weight as measured in atmosphere of 59% Hm. after treatment.
			Before treatment	After treatment (samples dried at air temperature)	
80	Diamond Black	1.25% gain	14.24%	14.19%	1.25% gain
81	Alizarin Navy	1.16% gain	,,	13.70%	0.69% gain
82	,, Fawn	0.15% loss	,,	13.06%	1.13% loss
83	,, Grey	0.56% loss	,,	13.50%	1.17% loss
84	,, Dark Blue	1.25% gain	,,	13.29%	0.52% gain
85	,, Nigger Brown	no change	,,	14.05%	0.09% loss
86	Diamond Black	0.97% gain	14.06%	14.31%	1.26% gain
87	Alizarin Navy	1.27% gain	,,	13.69%	0.98% gain
88	,, Fawn	0.20% loss	,,	13.32%	0.84% loss
89	,, Grey	0.37% loss	,,	13.60%	0.75% loss
90	,, Dark Blue	1.32% loss	,,	13.49%	0.85% gain
91	,, Nigger Brown	no change	,,	14.45%	0.40% gain

Milled—First six with soft soap. Second six with hard soap.

TABLE XI.—(Cotton Warp Shoddy Cloth).

No. of Sample	Treatment	Change in Dry Weight.
92	Acid Black and burl dye iron	4.39% gain
93	Logwood Black and burl dye iron	4.93% gain
94	Navy and burl dye iron	2.61% gain
95	Brown and cotton dyed	2.72% loss
96	Light Blue and cotton dyed	4.34% loss

TABLE XII.—(Tubular Hosiery).

No. of Sample	Treatment	Change in Dry Wt.	Regain in atmosphere of 59% Humidity. (72°F.) Before treatment	Regain in atmosphere of 59% Humidity. (72°F.) After treatment and complete finishing	% change of weight as measured in atmosphere of 59% Hm. After treatment and complete finishing	Regain in 59% atmosphere after wetting out	After second wetting out
56.S.	Xt. Scarlet 6 R. 3%	0.97% gain	13.81%	10.24%	1.90% loss	13.52%	—
57.S.	Dyed with 56 then stripped with 4% zinc formaldehyde hydrosulphite and 2% Formic Acid at boil for ½ hr. Scoured and re-dyed with Xt. Scarlet 6 R. 2%	0.94% loss	,,	10.94%	3.52% loss	13.06%	—
58.F.	Phenylamine Black 4B 3.5% boiling	0.86% gain	,,	10.54%	2.07% loss	13.74%	—
59	Chromed with: Sod. bichrome 1.5% for; Lignorosine .5% one; Formic Acid .5% hour.	2.59% gain	,,	11.42%	0.17% loss	14.30%	15.06%
60.S.	Then dyed with Hematine 4%, boil 1 hr. Putty: Xylen Light Yellow 2.G. .08%; Azo Geranine B. .03%; Solway Cyanine 3.F.L. .03%	0.99% loss	,,	10.68%	3.91% loss	13.15%	—
61.S.	Grey: Solway Cyanine 3.F.L. .06%; Azo Geranine B. .03%; Xylen Light Yellow 2.G. .03%	1.13% loss	,,	10.20%	4.30% loss	13.24%	—
62.S.	Tobac: Tartrazine .5%; Azo Geranine B. .2%; Solway Cyanine 3.F.L. .2%	0.87% gain	,,	10.23%	2.45% loss	13.20%	—
63.F.	Navy: Coomassie Navy Blue 2 RNX 2%; ,, Fast Black 1%	0.26% gain	,,	11.50%	1.90% loss	14.50%	15.00%

TABLE XII.—*continued.*

No. of Sample	Treatment		Change in Dry Wt.	Regain in atmosphere of 59% Humidity (72°F)		% change of weight as measured in atmosphere of 59% Hm. After treatment and complete finishing	Regain in 59% atmosphere after wetting out	After second wetting out
				Before treatment	After treatment and complete finishing			
64.S.	Green	Kiton Fast Green V. 2.5% Tartrazine .5%	0.42% gain	13.81%	10.20%	2.67% loss	12·83%	13.10%
65.S.	Saxe	Patent Blue V. .3% Azo Geranine B. .06% Orange 2 .04%	0.92% loss	,,	10.89%	3.55% loss	13.50%	—
66.S.	Coral	Azo Geranine B. .3% Orange 2 .1% Solway Cyanine 3.F.L. .015%	2.17% loss	,,	11.75%	5.82% loss	14.07%	—
67.S.	Nigger	Kiton Violet 10.B. .75% Orange 2 .75% Tartrazine .4% Wool Green S. .3% Azo Geranine B. .15%	2.89% gain	,,	10.43%	0.20% loss	12.71%	13.33%

The additions to the dyebaths were as follows :—

Nos. 56, 57, 60, 61, 62, 64, 65, 66, 67 were dyed with 1.5% H_2SO_4 and 20% Glauber Salts.

Nos. 58 and 63 were dyed with .5% Formic Acid and 20% Glauber Salts.

All dyeings were done at, or just under, the boil for 2—2½ hours. After dyeing the fabrics were washed off, hydro-extracted, dried, and pressed in the Pegg Press.

TABLE VI.—Appendix.

Initial Composition of Bath				% Acid left in bath (Experimental)	% Acid in Wool when in bath (calculated)	% Acid in Wool after washing off (Experimental)	% Acid washed off (calculated)	% change of Dry Wt. +=increase —=decrease	% change of Wt. in atmosphere of humidity room	Actual Regain [Initial Regain 15.54 first series 16.21 second series]
Number	% Acid	% Glauber Salt	% Dye (Crystal Scarlet)							
101	Distilled	Water	—	—	—	—	—	—1.05	—0.64	16.03
102	—	5	—	—	—	—	—	—1.00	—0.53	15.98
103	—	10	—	—	—	—	—	—1.27	—0.47	16.26
104	—	20	—	—	—	—	—	—1.11	—0.47	16.18
109	1.5	—	—	0.126	1.374	0.67	0.71	+0.12	+0.07	15.37
111	2.0	—	—	0.169	1.831	0.97	0.86	+0.42	+0.33	15.32
112	3.0	—	—	0.536	2.464	1.41	1.05	+0.92	+0.60	15.19
121	3.5	—	—	0.799	2.701	1.65	1.05	+0.87	+0.91	—
105	4.0	—	—	0.850	3.150	1.51	1.62	+0.81	+0.63	15.27
122	4.5	—	—	1.693	2.807	1.54	1.26	+1.08	+0.74	—
113	5.0	—	—	1.455	3.545	1.83	1.71	+1.30	+0.96	15.00
123	7.0	—	—	3.194	3.806	1.88	1.91	+1.46	+1.04	—
124	8.0	—	—	4.052	3.948	1.93	2.02	+1.69	+1.31	—
114	10.0	—	—	5.919	4.081	2.26	1.82	+1.32	+0.78	14.70
110	1.5	10	—	0.129	1.371	0.69	0.68	—0.27	+0.13	15.88
106	4.0	5	—	0.910	3.010	1.65	1.44	+0.92	+0.70	15.22
107	4.0	10	—	1.077	2.923	1.42	1.50	+0.73	+0.50	15.17
108	4.0	20	—	1.158	2.840	1.52	1.32	+0.42	+0.53	15.49
115	4.0	10	0.05	1.157	2.843	1.50	1.34	+1.00	+0.73	15.18
116	4.0	20	0.05	1.199	2.801	1.76	1.04	+1.40	+0.87	14.88
117	4.0	10	0.30	1.120	2.880	1.62	1.26	+1.46	+1.10	15.02
119	4.0	10	0.30	—	—	—	—	+1.39	+0.90	—
118	4.0	20	0.30	1.064	2.936	1.50	1.44	+1.27	+0.90	15.07
120	4.0	20	0.30	—	—	—	—	+1.52	+1.31	—
119	4.0	10	0.30	—	—	—	—	+1.39	+0.90	15.61
120	4.0	20	0.30	—	—	—	—	+1.52	+1.31	15.90
121	3.5	—	—	0.799	2.701	1.65	1.05	+0.87	+0.91	16.16
122	4.5	—	—	1.693	2.807	1.54	1.26	+1.08	+0.74	15.79
123	7.0	—	—	3.194	3.806	1.88	1.91	+1.46	+1.04	15.74
124	8.0	—	—	4.052	3.948	1.93	2.02	+1.69	+1.31	15.79

APPENDIX.

Note on the Results shown in Table VI.

The results shown in Table VI. give a much deeper insight into the processes investigated than do those shown in the other Tables.

As in the case of the previous experiments each sample was brought to the boil in half an hour, boiled for one hour.

The samples weighed about 30 grams each and were dyed in 1500 ccs. of liquor.

In order to get rid of the acid merely entangled in the fabric it was squeezed and rinsed once quickly in distilled water and squeezed again, the liquors being returned to the bath. The amount of acid remaining in the bath was then determined by titration.

The sample was then washed off for half an hour in a large volume of running tap water, and was allowed to dry without heat. At the conclusion of the conditioned weight determinations in the humidity room the sample was divided into two parts, one being dried out and the other titrated to determine the residual acid. The analyses of the acid in the fabric after dyeing are strictly comparable, but may all be subject to a slight correction due to the presence of fatty acid.

In this way we obtain values of (a) the amount of acid in the sample while in the bath, (b) the amount left in the bath, and (c) the residual acid in the cloth after washing..

There is a slight element of uncertainty as to the precise degree of preliminary rinsing necessary to remove the entangled liquor from the material. The amount of acid ultimately removed by the final half hour washing is, however, very much greater than the amount in the entangled liquor, so that this source of error is not a serious one. Thus in the case of the 10% of acid, since the sample weighed about 30 gm. and the volume of the liquor was about 1500 cc., the original acid solution was only a 0.2% solution and became a 0.1% solution at the end of the boil. Even if the wool had been allowed to retain its own weight of liquor it would have only led to an error of 0.1% in the value of the acid retained at the boil.

In Fig. 1 are plotted the original percentages of acid against the amount held by the wool (a) at the boil, (b) after washing off. The former quantity is roughly double the latter. Both curves show the same general trend : the amount taken up increasing at first very rapidly with the amount originally in the bath—the rate rapidly diminishing, however, and showing signs of ultimately approaching zero, i.e., the amount taken up tending to a constant value.

In Fig. 2 the amount taken up is plotted against the amount of acid left in the bath. This amount is expressed both as a percentage of the weight of the sample and as actual normality of acid solution. This latter value is only approximate since the final volume of liquor was not measured accurately.

These curves are typical adsorption curves—the ratio of the amount taken up to the concentration of liquor increasing enormously at low concentrations. The acid contents of the wool are by no means very small, but correspond to excessively low concentrations in the bath, so that, as is well known, wool may practically exhaust an acid bath. Conversely the curve shows why it is so difficult to remove the last traces of acid from wool by rinsing.

The additions to the bath (Glauber salt and dye) do not cause any marked effect on the relation between the amount taken up and the concentration of the bath. The amount taken up while the wool is in the bath does perhaps show a slight diminution though the effect is on the limit of experimental error.

In Fig. 3 the amount of acid retained after washing (as determined by titration) is plotted against the increased dry weight. If the acid formed a compound with the wool, or if it were absorbed as a whole, and if in addition there were no loss of wool substance, the points should be on a straight line O N through the origin inclined at 45° to the axes. If the loss is the same in all cases the points should lie on a straight line parallel to the above line, at a distance measured parallel to the vertical axis corresponding to the loss.

Now the points show considerable dispersion though the general trend is linear and not far from the 45° direction. The high degree of dispersion of the points evidently originates in the measurement of the loss of material—the acid in the wool may be measured quite accurately enough.

Applying the method of least squares* on the assumption that the errors lie mainly in the measurement of the increased weight, we obtain for the best straight line to fit the results, the line A B. This line makes an angle of 47° with the horizontal axis—an angle very near to the theoretical angle of 45°. The line corresponds to a loss of material varying from 0.74% in a bath of acid containing just enough to neutralise the wool, to 0.56% in the strongest bath used.

Whether this deviation of the direction from 45° (including the resultant implication that the loss of wool substance diminishes with increase of acid) has any meaning, must be regarded as an open question in view of the relatively large experimental errors. The line D E drawn at 45° through the centroid of the points, gives practically as good a fit as A B. This line corresponds, of course, to a constant loss of wool substance equal to the average difference between the numbers in columns 7 and 9 of Table VI., not including, of course, the first four values in Column 9, and the incomplete data relating to Samples 119 and 120.

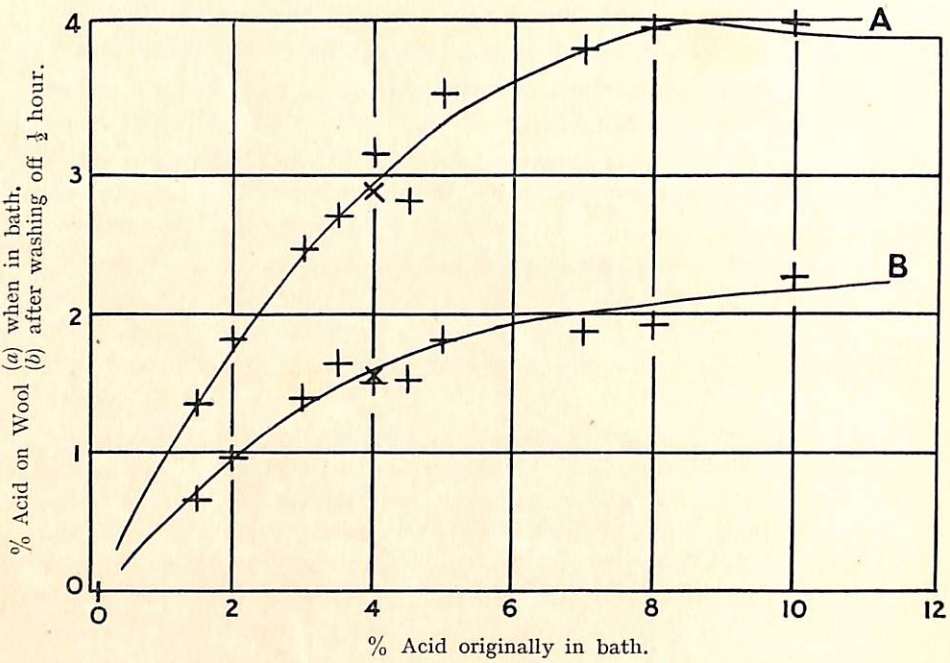
The goodness of fit of the line D E is a satisfactory confirmation of the general accuracy of the experimental results. The results may

* The points corresponding to dyed specimens have been lowered by an amount equal to the percentage of dye. The two stars indicate the uncorrected position with 0.3% dye.

be summarised by saying that when wool is boiled and washed off in the manner adopted in the present experiments the gain in dry weight is equal to the weight of acid taken up (as determined by titration) minus 0.6* (all the quantities being expressed as percentages of the weight of the wool). This rule will be correct within the limits of the series of experiments. With very small amounts of acid the change of weight may be less than is given by the rule. With the small amount of acid required just to make the wool neutral the loss will probably be nearly equal to loss obtained by boiling with water (1%).

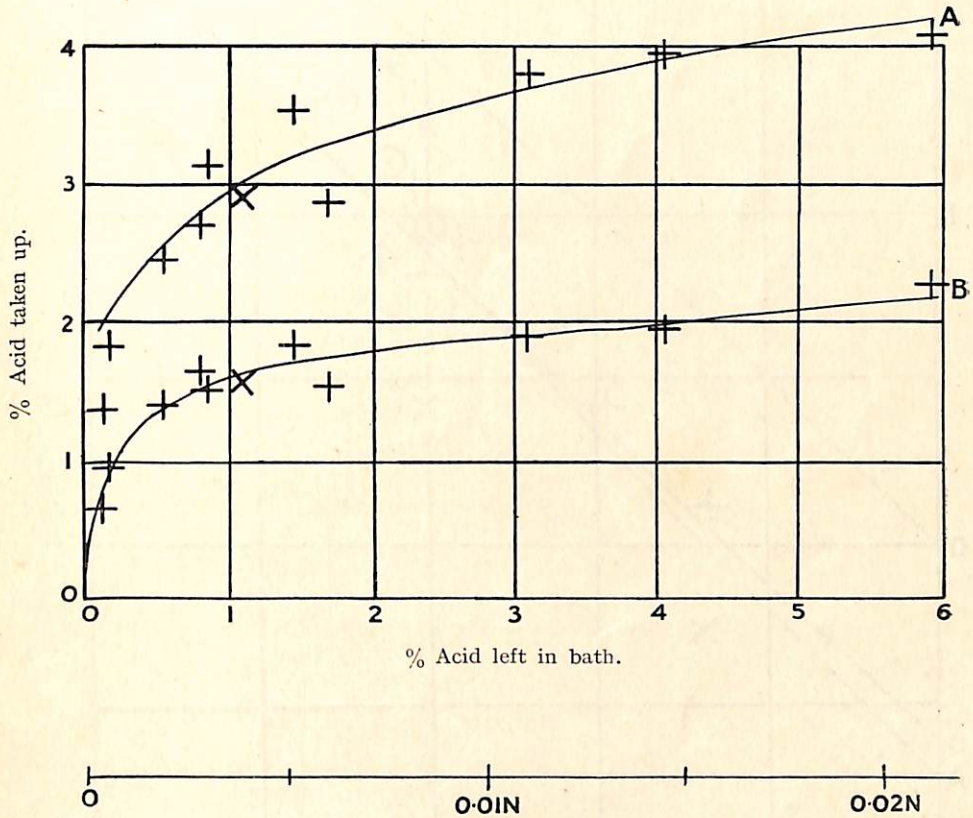
* The 0.6 represents wool substance, soap residues, etc., lost or destroyed.

Fig. 1.



NOTE.—The St. Andrew crosses (×) denote the positions of the mean values of the acid on the wool for all the samples treated with 4% Acid and Glauber salts or dye. Putting in the eight points for each curve would have led to confusion.

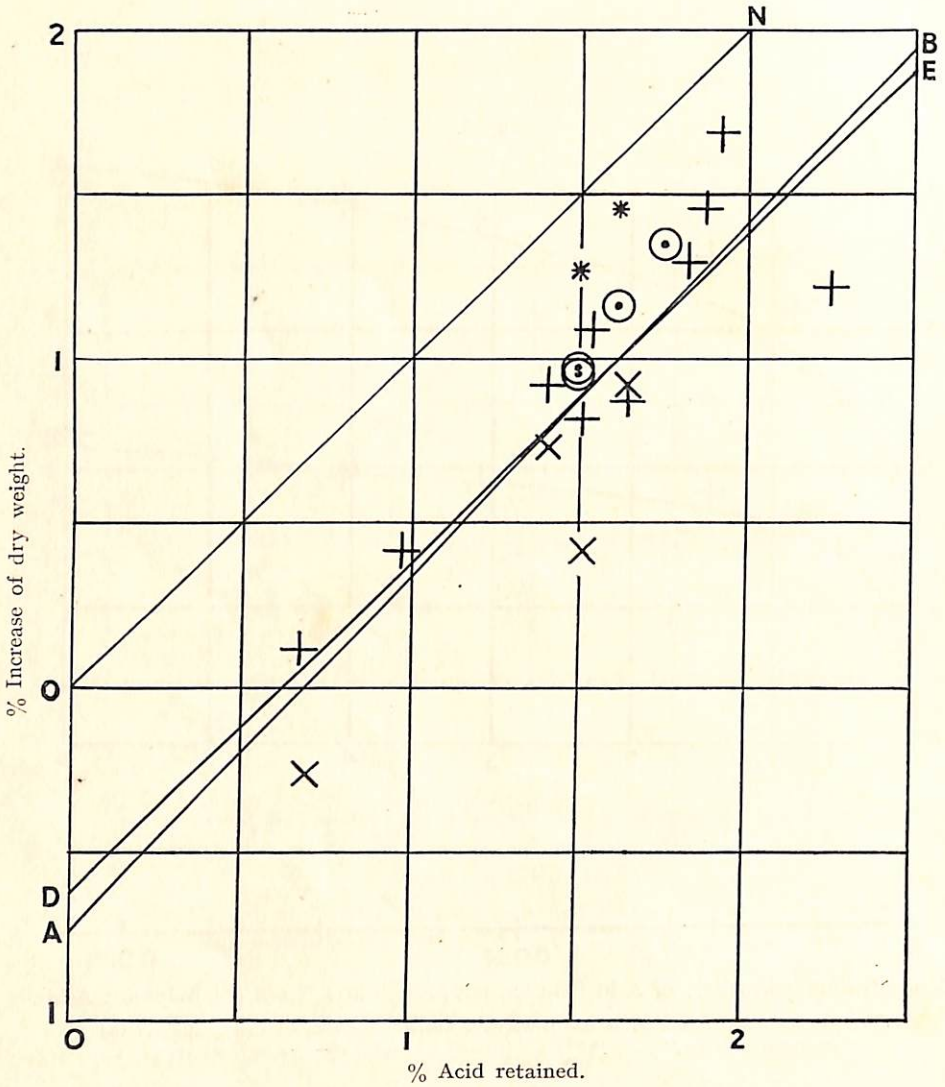
Fig. 2.



Concentration (normality) of Acid Solution left in bath (0·1 N.=2·8% Sulphuric Acid).

NOTE.—The curve for the amount of acid taken up at the boil has been drawn according to the "adsorption equation," $y=2.95\sqrt[5]{x}$ (y= % acid taken up: x= % acid left in bath).

Fig. 3.



NOTE.—The results relating to sulphuric acid alone are shown by a St. George cross (+), those relating to the addition of Glauber salts by a St. Andrew cross (×), and those relating to dyes by a circle. In the case of the latter the values of the increase of weight have been decreased by the amount of dye. The two stars show the uncorrected position of the points corresponding to the samples with 0.3% of dye.

Stembridge & Co. Ltd., Printers, Top of Albion Street, Leeds